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## Grain Size Dependent Magnetic Properties of Nanocrystalline $\text{Sm}_2\text{Co}_{17}/\text{Cu}$

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### ABSTRACT

The evolution of both micro structural and magnetic properties of the  $\text{Sm}_2\text{Co}_{17}-\text{Cu}$  powder, is studied as a function of soft co-milling time. The average grain size in the range 20 - 50 nm was determined by transmission electron microscopy coupled with x-ray diffraction using the Rietveld method. The particle shape and chemical distribution were investigated by elemental mapping, using wavelength dispersive x-ray analysis with electron microprobe analysis. The coercivity evolution shows that an optimum value of 6 kOe is obtained after 5 h co-milling. The microstructure analysis indicates that both materials are well mixed in nanometer scale. This technique appears as a potential route to synthesize nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  isolated by non-magnetic metal Cu.

### INTRODUCTION

Tremendous interest in the binary rare-earth transition metal (RE-TM) alloys exists because of their superb magnetic properties [1]. Most commercial high strength magnets are made from either the binary compound  $\text{SmCo}_5$  or the compound  $\text{Sm}_2\text{Co}_{17}$ . New core-shell structure as  $\text{Sm}_2\text{Co}_{17}/\text{Cu}$  presents a great interest in the magnetic recording field. High-density storage material requires small magnetically independent particles above their superparamagnetic critical diameter (lower than 20 nm). Thus the powder coating process seems to be an appropriate way to obtain isolated ferromagnetic particles. Magnetic nanostructures often exhibit distinctly different behavior than their bulk counterparts [2]. The ideal medium for high-density magnetic recording with low noise consists of magnetically isolated nanoscale grains [3,4]. For such small grain high magnetocrystalline anisotropy is needed to avoid the magnetization fluctuation caused by thermal effect and demagnetizing field. In the last few years, Sm-Co system has received considerable attention due to the high anisotropy [5,6]. In order to magnetically isolate the grains different solutions have been proposed such as physical separation of the grains [7] and segregation of a nonmagnetic phase at the grain boundaries [8]. Current studies have investigated Sm-Co particles prepared by annealing Sm-Co thin film on different substrates and under layers. This study deals with the grain size dependence of magnetic properties of nanocrystalline  $\text{Sm}_2\text{Co}_{17}$  particle soft co-milled with Cu nanoparticles in order to get potential candidates for magnetic recording. The requirements for such goal are monodomain magnetically isolated grains of 20 to about 50 nm with magnetization  $\mu_0 M_s \sim 0.5$  T and coercivity  $H_C \sim 5$  kOe. The special choice of  $\text{Sm}_2\text{Co}_{17}$  results from its semi-hard magnetic character.

### EXPERIMENTAL DETAILS

The intermetallic  $\text{Sm}_2\text{Co}_{17}$  was prepared by mechanical alloying technique. High-purity powders Sm (99.99%) and Co (99.8%), were used. All chemicals were handled inside a glove box under high-purity argon gas. They were carefully weighed, in the stoichiometric ratio 2:17, inside the box to give SmCo mixtures, and placed immediately into stainless steel jars. Next the powders

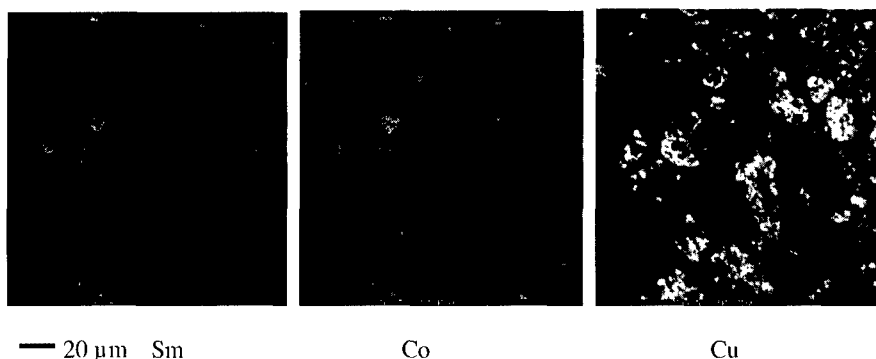


Figure 1: The image of element mapping of  $\text{Sm}_2\text{Co}_{17}$ -Cu co-milled 30 min.

were ball-milled in a high energy (power 10) Fritsch P7 planetary ball mill to form an ultra-fine layered microstructure. The mixtures were sealed in hardened steel vial together with five 15 mm diameter steel balls. A ball to powder mass ratio of 15:1 was used with milling time of 5 hours. The as-milled powder were wrapped in Tantalum foil and sealed into silica tubes under a vacuum of  $5 \times 10^{-7}$  Torr, then annealed at 800 °C for 30 min. Particle size was reduced by means of hydrogenation-deshydrogenation technique (HD)

$\text{Sm}_2\text{Co}_{17}$  powder and Cu nanoparticles, produced by cryogenic melting technique [9], were soft co-milled using the same planetary miller but with power 5 and 25 steel balls with diameter 7.3 mm. The milling time was varied from 30 min to 5 hours. The particle shape and the chemical distribution of samples milled 30 min, 2h and 3h were investigated by elemental mapping using wavelength dispersive x-ray analysis by electron microprobe analysis (EPMA).

Bright-field transmission electron micrographs (TEM) were taken using a JEOL 2010 high-resolution microscope operating at 200 kV. TEM sample preparation consisted of encapsulating milled powder in a room-temperature-cured epoxy and microtoming with a diamond knife to a thickness of approximately 100 nm.

The crystal structure was deduced from x-ray-diffraction (XRD) patterns, registered on a Bruker diffractometer with automatic divergence slit ( $\text{CuK}\alpha$  radiation  $\lambda = 1.54178 \text{ \AA}$ ). The grain size of the sample was determined from XRD patterns using Rietveld method.

The magnetic properties of all samples were measured using a vibrating sample magnetometer equipped with a 7 T superconducting magnet in Max-Planck-Institute for Metal Research, Stuttgart, Germany.

## DISCUSSION

After annealing the as-milled (Sm,Co) powders, the Rietveld analysis confirms the existence of hexagonal  $\text{Sm}_2\text{Co}_{17}$  with  $P6/mmm$  space group. The diffraction crystallite size (DCS) is around 50 nm. From scanning electron microscopy (SEM) the particle size is evaluated in the range of 20  $\mu\text{m}$ . One particle should contain a large number of crystallites. Afterwards, the particle size is reduced down to 5 - 10  $\mu\text{m}$  by HD technique. The final magnetic characteristics are obtained by further soft co-milling with Cu: (i) reduction of crystallite size at most down to 20 nm (ii)

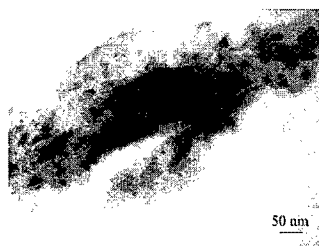


Figure 2: Transmission electron micrograph of  $\text{Sm}_2\text{Co}_{17}$ -Cu co-milled 2 h.

separation and coating of  $\text{Sm}_2\text{Co}_{17}$  crystallite.

The EPMA images for samples with Cu co-milled half an hour are shown, as an example, in figure 1. It can be deduced that the particle size of  $\text{Sm}_2\text{Co}_{17}$  reduces monotonously from about  $10\ \mu\text{m}$  for sample milled 30 min to  $1\ \mu\text{m}$  for samples milled 2 h. For the sample milled 2 h, the  $\text{Sm}_2\text{Co}_{17}$  particles are homogeneously separated by Cu particles. Figure 2 shows the TEM micrograph for the sample milled 2 hours. The TEM investigation shows that the grain size is in the range of 10-20 nm. The EDX analysis carried out by TEM did not show neither a region of pure  $\text{Sm}_2\text{Co}_{17}$  nor pure Cu. This indicates that the materials are well mixed in nanometer scale. The XRD patterns of all samples can be indexed by hexagonal  $\text{Sm}_2\text{Co}_{17}$  with additional cubic Cu phase. After soft co-milling with Cu nanoparticles,  $\text{Sm}_2\text{Co}_{17}$  powder keeps hexagonal  $P6/mmm$  structure but with much broader reflections. The DCS and the microstrain rate have been determined from x-ray diffraction patterns using Rietveld method. The obtained  $\text{Sm}_2\text{Co}_{17}$  DCS is plotted as a function of milling time and shown in figure 3. The grain size of  $\text{Sm}_2\text{Co}_{17}$  decreases monotonously with milling time whereas the grain size of Cu remains constant. One can notice from figure 3 a slow decrease of  $\text{Sm}_2\text{Co}_{17}$  grain size from 2 h to 5 h of co-milling time. This behavior means that it is possible to reduce the DCS to within 20 nm a value required for the high-density magnetic recording.

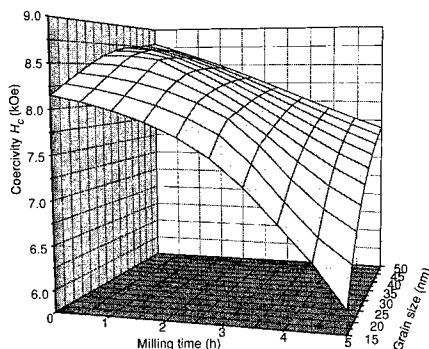


Figure 3: The dependence of room temperature coercivity ( $H_C$ ) on  $\text{Sm}_2\text{Co}_{17}$  grain size and co-milling time.

The room temperature hysteresis loop for sample before co-milling and after 5 hours co-milling are comparatively shown in figure 4. The room temperature coercivity ( $H_C$ ) and remanence ratio ( $M_r/M_s$ ) as a function of co-milling time is illustrated in figure 5. It can be seen that  $M_r/M_s$  decreases rapidly from the 0.58 for the unmilled powder down to 0.52 after only half an hour milling. Then, with milling time, it decreases slightly to 0.5 for 5 h milled powder. On the contrary, the coercivity keeps almost constant at the beginning of milling. After 1 h milling  $H_C$  decreases monotonously from 8.6 kOe to 6.0 kOe for sample milled 5 hours. This value is an optimum value for magnetic recording application. The powder after 5 hours co-milling possesses suitable magnetic and microstructure properties (magnetically separated grains) for high-density recording application.

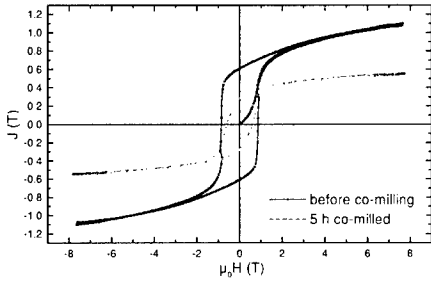


Figure 4: Hysteresis loops of co-milled  $\text{Sm}_2\text{Co}_{17}\text{-Cu}$  powder.

From figure 3 it can be seen that the coercivity remains constant as the grain size decreases from 50 nm before co-milling to 30 nm after 1 h co-milling.  $H_C$  decreases rapidly with further decreasing grain size. Two competing effects can explain this: the co-milling refines the grain size and reduces the coercivity. However, meanwhile the co-milling breaks the exchange coupling between the grains (which is proved by the reduction of  $M_r/M_s$ ), it tends to enhance the coercivity.

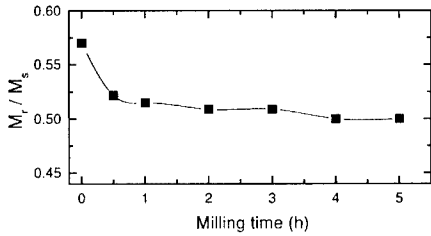


Figure 5: The dependence of the remanence ratio  $M_r/M_s$  on co-milling time.

After 1 h milling the exchange coupling between grains is completely broken, further reducing grain size, from 30 nm to 10 nm, leads to decreasing the coercivity. For a fine particle system, the decrease in  $H_C$  with decreasing grain size is due to thermal effect. Hence, the temperature dependence of the coercivity should obey the  $H_C \propto T^{1/2}$  law. The coercivity of sample milled 5 hours at different temperature are obtained and plotted as a function of  $T^{1/2}$  in figure 6. It shows a linear relation between  $H_C$  and  $T^{1/2}$ , and indicates that the reduction of coercivity for small grain size (see figure 4) is a consequence of thermal effect, and 15 nm is near the superparamagnetic limit for  $\text{Sm}_2\text{Co}_{17}$  powder.

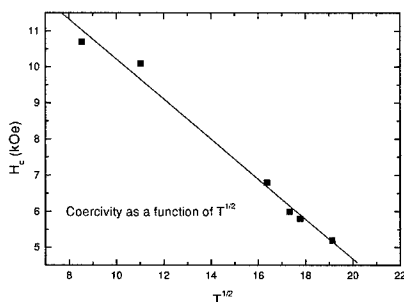


Figure 6: The coercivity for 5 h milled sample as a function of  $T^{1/2}$

## CONCLUSION

- \* After soft co-milling with Cu nanoparticles, nanocrystalline Sm-Co powder remains hexagonal with  $P6_3/mmm$  structure.
- \* The diffraction crystallite size of  $\text{Sm}_2\text{Co}_{17}$  decreases from 50 nm before co-milling down to 15 nm after 5 h co-milling.
- \* TEM shows that the grain size is in the range of 10 - 20 nm after 5 h co-milling. The material is well mixed in nanometric scale, consistent with the DCS study.
- \* The coercivity decreases to 6.0 kOe after 5 h co-milling.
- \* By co-milling with Cu nanoparticles, the microstructure as well as the magnetic properties of  $\text{Sm}_2\text{Co}_{17}$ -Cu powder can be controlled by milling conditions. Thus, this technique is a potential way to synthesize nanocomposite  $\text{Sm}_2\text{Co}_{17}$ -Cu particles isolated by non-magnetic metal Cu with suitable magnetic properties and microstructure for high-density recording.

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